# 1866772 - R8 SDMS

# RICO ARGENTINE ST. LOUIS PONDS SITE EVALUATION OF SURFACE WATER METAL CONCENTRATIONS

This technical memorandum includes discussion and graphs of water quality data related to the Rico Argentine St. Louis Ponds site in Rico, Colorado. An evaluation of water quality measured in the Dolores River from April 1998 through April 2012 is presented first, followed by an evaluation of water quality at the St. Louis Tunnel discharge and the pond system outfall.

The data are discussed in light of regulatory and potential permit standards developed by the State of Colorado. These include:

- Standards for the Dolores River established by the Colorado Department of Public Health and Environment, Water Quality Control Division (WQCD) can be found at 5 CCR 1002-34, Regulation No. 34 Classifications and Numeric Standards for San Juan River and Dolores River Basins Revised (<a href="http://www.cdphe.state.co.us/regulations/wqccregs/">http://www.cdphe.state.co.us/regulations/wqccregs/</a>). Regulation 34, Dolores River Basin stream segment 3 is applicable to the Dolores River in the area under discussion. Revised standards have been proposed for stream segment 3 as discussed below.
- Table value standards (TVS) are standards frequently applied to state stream segments are presented in Regulation No. 31. Changes to the chronic and acute zinc TVS have been proposed as discussed below. Many of the TVS are hardness-based standards.
- A water quality assessment (WQA) of the Dolores River near the St. Louis Tunnel discharge was developed by the WQCD. The WQA was prepared to facilitate issuance of a Colorado Discharge Permit System (CDPS) permit for the St. Louis Tunnel, formerly covered under CDPS Permit No. CO-0029793, and was intended to determine the water quality-based effluent limits (WQBELs) and anti-degradation-based average concentrations (ADBACs) available to the St. Louis Tunnel discharge for pollutants found to be of concern. The assessment provided potential effluent limits for the discharge of the St. Louis Tunnel. The WQA used estimated flows in the Dolores River and pond discharge and concentrations of contaminants in upstream Dolores River water to calculate allowable concentrations of contaminants in site discharges. The WQA used a hardness level of 247 mg/L for calculating hardness-based standards; therefore, that is the value that was used to calculate the standards referenced in this document.

# Water Quality in the Dolores River

Dissolved cadmium, manganese, and zinc concentrations in the Dolores River are presented on Graphs 1 through 9. The graphs show concentrations in Dolores River water upstream of the site (DR-1), immediately upstream of the pond outfall (DR-2), downstream of the site (DR-7), and farther downstream (DR-4SW and DR-G). Other contaminants were not graphed because they were not detected in the bulk of site samples, data was not available, or because all data were below a level of concern related to the standards being discussed. The current (cadmium) or proposed (manganese and zinc) water quality standards are shown on the Dolores River graphs. Data from 1998 through April 2012 are presented, with the greatest number of sample results (monthly sample results) being from April 2011 through April 2012. For clarity some graphs focus on the current Atlantic Richfield data from December 2010 through April 2012. The detection limit is shown for data points where an analyte was not detected by laboratory analysis.

# **Dissolved Cadmium**

- Cadmium concentrations at DR-7, located downstream of the St. Louis Ponds site, typically exceeded the chronic WQS during moderate- and low-flow periods, and concentrations at the other locations downstream exceeded WQS during low-flow periods (Graphs 1 through 3).
- Cadmium concentrations were not detected above the acute WQS.
- The dissolved cadmium graphs are illustrative of site conditions for the most part; however, elevated cadmium concentrations in July 2002 and April 2011 are the result of a high detection limits, not necessarily elevated cadmium concentrations.
- No long-term trends were identified in the dissolved cadmium data.

#### **Total Iron**

• Total iron concentrations infrequently exceeded the total iron WQS at DR-7, but during some instances, the concentrations were higher at upstream locations than at DR-7 (Graphs 4 through 6).

# Dissolved Manganese

- The proposed dissolved manganese WS standard was not exceeded at DR-1, located upstream of the St. Louis Ponds site except in the October 1999 sample, but was exceeded at sample location DR-7, downstream of the St. Louis Ponds, at all times of year. Manganese concentrations exceeded the proposed WS standard at DR-2 and at downstream locations during moderate- and low-flow periods (Graphs 7 through 9).
- Manganese concentrations in the Dolores River appear to be higher during low-flow times of year than during spring runoff.
- No long-term trends were identified in the dissolved manganese data.

# Sulfate

- Sulfate concentrations did not exceed the proposed WS standard at any locations (Graphs 10 and 11).
- Sulfate concentrations were higher near the Silver Swan discharge downstream of the site (DR-4SW) than immediately downstream of the St. Louis ponds outfall (DR-7).
- Sulfate concentrations in the Dolores River appear to be higher during moderate- and low-flow than during highflow.

# Dissolved Zinc

- The available dissolved zinc data indicate that the proposed zinc WQS was rarely exceeded at any of the Dolores River monitoring locations (Graphs 12 through 14).
- Zinc concentrations appear to be higher during low-flow periods than during spring runoff.
- Seasonal trends were stronger than long-term trends in the available dissolved zinc data, but zinc concentrations measured at DR-7 in 2010-2012 appear somewhat higher than those detected from 1998 through June 2003.

# Water Quality in St. Louis Ponds

St. Louis Tunnel discharge (DR-3) and St. Louis Ponds outfall (DR-6) water quality data from 2002 through April 2012 are presented on Graphs 15 through 35. WQBELs or WQS are shown on the graphs for comparison. The percent removal of the metals in the pond system is presented to allow comparison of conditions over time, particularly seasonal variations and variations potentially attributable to recent site work.

# **Dissolved Cadmium**

- Dissolved cadmium concentrations in the St. Louis Tunnel discharge and the pond outfall exceeded the WQS for the Dolores River and generally exceeded the WQBEL (2.3 μg/L) (Graphs 15 through 19).
- The pond system outfall cadmium concentrations were typically 4 to 5 times the WQBEL during low flow periods, but were 10 to 22 times the WQBEL during high flow periods. The higher concentrations during high-flow periods are offset by higher flows of water in the Dolores River such that dramatic increases in Dolores River metal concentrations are not seen during high flow (see Graphs 1 through 3). In fact, cadmium concentrations in the Dolores River downstream of the site are typically lower during high-flow periods than during fall and winter months.
- The percent removal of cadmium within the ponds is currently less than 50 percent (average of 31 percent since June 2010) and was as low as 21 percent removal during the July 2011 sampling event. The percent reduction values do not appear related to season or 2011 site work. The greatest percent reduction values were observed in the early 2000s.

# Dissolved Iron

- Dissolved iron concentrations in the St. Louis Tunnel discharge exceeded the proposed water supply standard for the Dolores River (300 µg/L), but the concentrations in the pond outfall generally did not exceed the proposed standard, providing an indication that iron discharges from the site likely will not adversely affect Dolores River water quality if the pond system is maintained (Graphs 20 through 22).
- Most of the dissolved iron discharging from the St. Louis Tunnel is removed in the ponds. The zero percent removal shown for April 2012 is due to both the St. Louis Tunnel discharge and the pond outfall containing undetectable amounts of dissolved iron.

#### Dissolved Manganese

• Dissolved manganese concentrations in the St. Louis Tunnel discharge and the pond outfall were generally similar

- to or lower than the WQBEL established in the WQA (2229 µg/L) (Graphs 23 through 27).
- The lowest dissolved manganese concentrations were recorded in 2002 and 2003, with greater concentrations measured in later years.
- Less seasonal variation was observed in dissolved manganese concentrations than in dissolved cadmium and zinc concentrations.
- Percent removal of manganese in the ponds was relatively high (68 to 84 percent) during 2002 and 2003 and decreased to less than 40 percent since December 2010.

# Sulfate

- Sulfate concentrations in the St. Louis Tunnel discharge and the pond outfall generally exceeded the proposed water supply standard (250 μg/L), providing an indication of potential influences on Dolores River quality (Graphs 28 through 30). A WQBEL for sulfate was not established in the WQA.
- The percent removal of sulfate within the ponds is negligible.

# Dissolved Zinc

- Dissolved zinc concentrations in the St. Louis Tunnel discharge and the pond outfall generally exceeded the WQBEL (729 μg/L) (Graphs 31 through 35).
- The pond system outfall cadmium concentrations were typically 3 to 5 times the WQBEL during low flow periods, but were up to 11.5 times the WQBEL during high flow periods. The higher concentrations during high-flow periods are offset by higher flows of water in the Dolores River such that dramatic increases in Dolores River metal concentrations are not seen during high flow. Conversely, zinc concentrations in the Dolores River downstream of the site are typically slightly lower during high-flow periods than during fall and winter months.
- The percent removal of zinc within the ponds is currently less than 50 percent (average of 30 percent since June 2010) and was as low as 7 percent removal during the October 2011 sampling event.
- The lowest percent reduction values were observed during the same period as the 2011 site work.
- The greatest percent reduction values were observed in the early 2000s.

# Proposed Changes to Colorado Water Quality Standards

Proposed changes to Colorado WQS for the main stem of the Dolores River from Horse Creek to Bear Creek (COSJDO03) include the following:

- 1. The classification of the stream will be changed to include water supply use. This change affects several standards. Specifically listed are the following (standards are for dissolved metals unless noted):
  - a. Nitrate standard of 10 mg/L
  - b. Chloride standard of 250 mg/L
  - c. Sulfate standard of 250 mg/L
  - d. Chronic arsenic standard of 0.02 µg/L
  - e. Acute chromium III standard of 50 µg/L
  - f. Chronic dissolved iron standard of 300 µg/L
  - g. The chronic manganese standard would be reduced from the aquatic use standard of 2229  $\mu$ g/L (calculated at hardness 247 mg/L, see below) to the water supply standard of 50  $\mu$ g/L.
- 2. The temperature standard was revised.
- 3. A chronic chromium III standard was added [Table Value Standard (TVS), 155 µg/L when calculated at hardness of 247 mg/L]. This value is higher than the acute water supply standard listed above.
- 4. A chronic molybdenum standard will be added (160 µg/L).
- 5. Acute and chronic zinc standards will be updated to the new TVS.
  - a. When calculated at hardness of 247 mg/L (as proposed by WQCD in the WQA), the acute standard increases from 310 μg/L to 364 μg/L and the chronic standard increases from 269 μg/L to 276 μg/L.

The following discussion presents potential impacts of the proposed changes based on site water quality as measured in the past 10 years.

- 1. Addition of the water supply designation would have an impact on site requirements.
  - a. Nitrate is not currently measured at the site, but the site is not expected to contribute nitrate at levels that

- would cause exceedances in the Dolores River. This would need to be reconsidered if certain water treatment technologies (e.g., a sulfate reducing bioreactor) are implemented.
- b. Chloride is not currently measured at the site, and the site is not expected to contribute chloride at levels that would cause exceedances in the Dolores River.
- c. The new sulfate standard of 250 mg/L was exceeded at the pond outfall (DR-6) in all recent samples (DR-6 samples 2010-2012 ranged from 531 mg/L to 976 mg/L) (Figures 23 through 25). A WQBEL was not established for sulfate in the WQA, but a CDPS standard might be developed by the state based on the new sulfate standard.
- d. The new chronic arsenic standard is problematic. The proposed dissolved arsenic standard of 0.02 μg/L is below the detection limit established in the Atlantic Richfield Sampling and Analysis Plan for Surface Water Sampling (SAP) of 0.09 μg/L and below reasonably achievable laboratory detection limits. The detection limit achieved by the laboratory for samples analyzed since April 2011 has been 0.5 μg/L, a relatively low detection limit even for drinking water rather than surface water. Common detection limits for drinking water analysis using ICP-AES are 2 μg/L to 10 μg/L. GFAA analysis can detect arsenic concentrations as low as 0.5 μg/L and 1.0 μg/L. Therefore, even detecting arsenic, much less being confident in the measured concentration, at the standard of 0.02 μg/L seems unlikely. Arsenic concentrations measured in the Dolores River at DR-7, immediately below the pond outfall, have ranged from non-detect at 0.5 μg/L to 1 μg/L. Dissolved arsenic was not found above the detection limit of 0.5 μg/L in the St. Louis Tunnel discharge from June 2010 through April 2012. Due to the very low standard relative to the detection limit and the absence of detectable dissolved arsenic in the St. Louis Tunnel discharge, it is unknown whether the new standard would be exceeded in the Dolores River due to site discharges.
  - i. The WQBEL presented in the WQA is 21 μg/L (total recoverable) based on the chronic aquatic life standard of 7.6 μg/L. The background concentration used in the WQA was 0.325 μg/L. Total recoverable arsenic was detected in the January and February 2012 samples in the St. Louis Tunnel discharge (DR-3) at levels much lower than the WQBEL (0.69 μg/L and 1.1 μg/L in January and February 2011, respectively), but not in the other 2011 2012 samples or at the pond outfall (DR-6).
- e. Total and dissolved chromium concentrations in the St. Louis Tunnel discharge and the pond outfall are much lower than the proposed standard for chromium III, so the new chromium III standard is not expected to impact site discharge limits.
- f. The proposed chronic iron water supply standard of 300 μg/L (dissolved) is a decrease from the previous 1000 μg/L (total recoverable) standard that was based on aquatic life criteria. The total iron WQBEL established in the WQA was 2719 μg/L. Total iron concentrations in the St. Louis Tunnel discharge ranged from 3140 μg/L to 13,000 μg/L between December 2010 and April 2011. During the same time period, total iron concentrations at the pond outfall ranged from 360 μg/L to 3900 μg/L. Dissolved iron concentrations in the pond outfall were much lower than total iron concentrations, ranging from not detected at 50 μg/L to 1900 μg/L. The 1900 μg/L concentration measured during December 2010 was significantly higher than the remaining 11 samples in the data set, the remaining samples averaged 93 μg/L. It is likely that reasonable controls on the pond effluent would allow the dissolved iron concentration standard to be met not only in the Dolores River, but also in the pond outfall water.
- g. The proposed water supply manganese standard of 50 µg/L is significantly lower than the chronic aquatic life standard of 2229 µg/L and lower than current water quality in the Dolores River at and downstream of the site (Graphs 23 through 27). Dissolved manganese concentrations generally did not exceed the Colorado water supply (WS) standard upstream of the site but did exceed the WS at sample location DR-7, downstream of the St. Louis Ponds site. Manganese concentrations exceeded the water supply standard at DR-2 and downstream locations during moderate and low flow periods. The water supply standard was not exceeded at DR-1, located upstream of the St. Louis Ponds site except in the October 1999 sample. Application of the water supply manganese standard to this stream segment and to potential discharge limits could have an impact on selection and implementation of water treatment technologies for the St. Louis Tunnel discharge. Dissolved manganese concentrations at DR-3 averaged greater than 2500 µg/L from April 2011 to April 2012. Many water treatment systems, including lime treatment and anaerobic cells, do not reliably remove manganese from the water. A separate operation for manganese removal may be required to meet the new standard.
- 2. The new temperature standard could impact site operations. The water discharged from the St. Louis Tunnel

averaged 15.3°C (maximum 20.6°C in July 2011) and the temperature of the pond outfall averaged 10.2°C (maximum 25.4°C in July 2011) from December 2011 through April 2012. The maximum weekly effluent discharge temperature established in the WQA based on the previous stream standard of 20°C was 27.5°C. Given that the maximum pond outfall temperature was within 2 degrees of the discharge limit, the new temperature standard could have an impact on the ability to meet potential new discharge limits.

- 3. The proposed acute chromium III standard based on water supply is less than the proposed chronic chromium III standard not related to water supply, so this proposed standard is not expected to impact site decisions.
- 4. Molybdenum is not on the current analyte list in the SAP; therefore, the implications of the new standard are unknown.
- 5. The proposed zinc standards are higher than the current standards and should allow slightly higher discharge zinc concentrations relative to the WQBEL presented in the WQA; however, the new chronic zinc standard is close to the previous standard, to the change will not significantly affect site discharge allowances. Comparison of the Dolores River zinc concentrations to the proposed standards is shown on Graphs 31 through 35.





































































